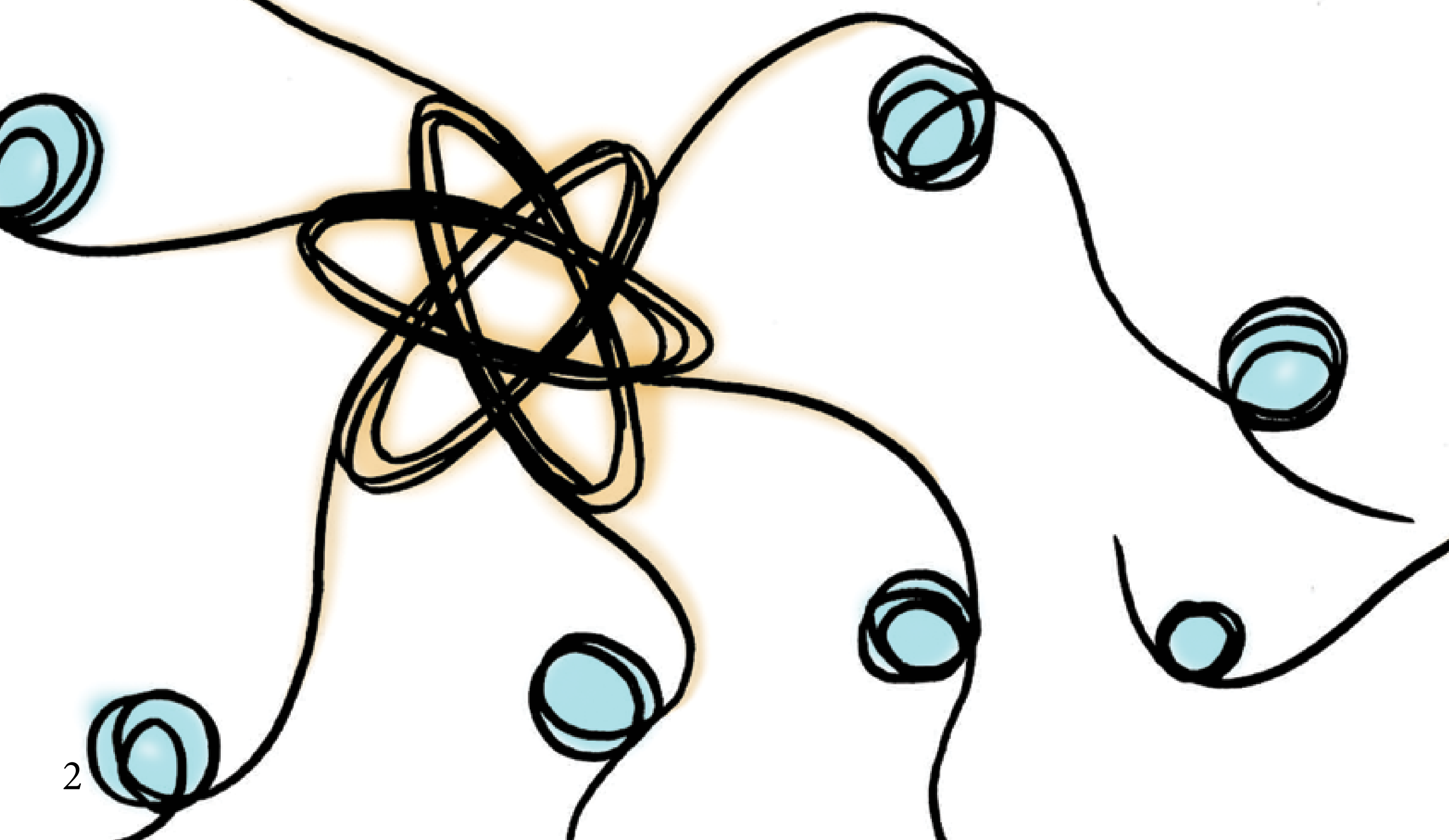
A Community of Electrons

When Los Alamos scientists solved the decades-long mystery of plutonium's missing magnetism, they got more than they bargained for: a groundbreaking insight into the overall nature of matter.



PLUTONIUM OUGHT TO PRODUCE MAGNETISM. Physicists and physical chemists have known this for more than 50 years. The orbital motion and intrinsic spin of electrons in plutonium atoms should conspire to create tiny loops of electrical current like miniature electromagnets. These should line up in an ordered array of magnetic atoms to make the material magnetic overall. Indeed, convincing theories have emerged to explain all six of solid plutonium's allotropes—sub-phases arising at different temperatures, each with its own distinct appearance and behavior—and those theories, too, provide for overall magnetism. All of this would make for a lovely scientific success story if plutonium metal were actually magnetic.

Instead, experiment after experiment shows the same thing: no detectable magnetic order. For more than half a century, this missing magnetism has remained a troubling curiosity. After all, here is an element of tremendous importance to nuclear weapons and several other essential technologies, which the government goes to great lengths to master in every detail, and yet, decade in and decade out, the best minds in the business are forced to go about their work with the nagging certainty that they've got something manifestly wrong.

Still, there's no need to duck and cover until a credible authority on plutonium says it's safe to come out—or even if there had been such a need, there isn't any more. The Los Alamos and Oak Ridge national laboratories and external collaborators have put forth new research, referred to by the Program Chair for the last international Plutonium Futures conference as "the most significant measurement on plutonium in a generation," resolving the missing-magnetism problem. The result is certain to benefit plutonium applications in important ways. Yet it is also broader than that. It is the key to a deeper understanding of other complex elements and compounds with distinctive electronic properties, and as such, it opens the door to a new era of advanced materials.

Beyond the simple solid

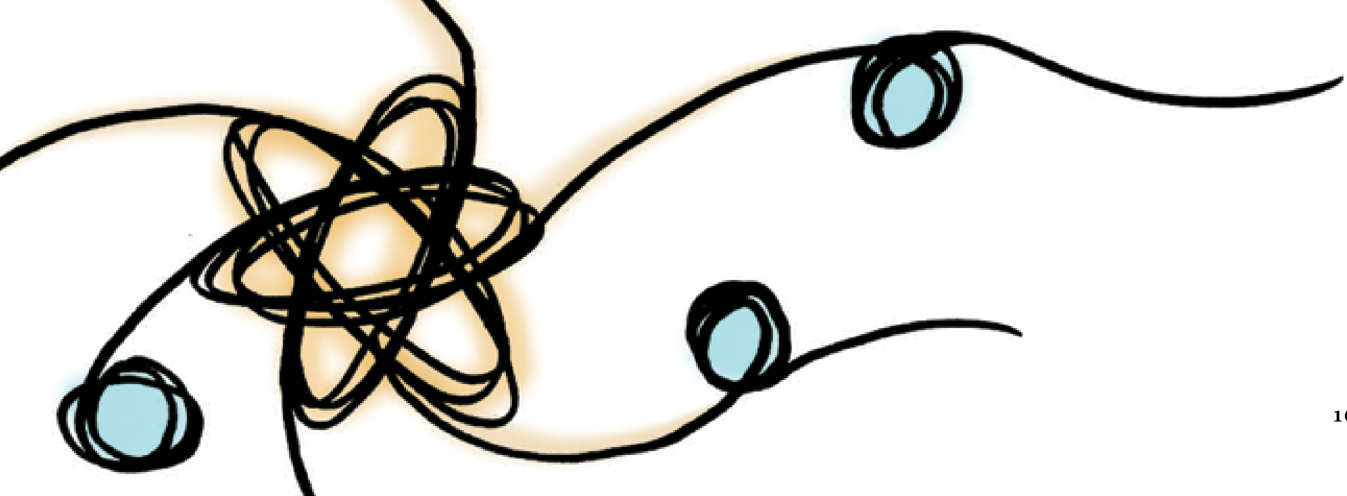
The standard lore taught to chemistry students goes like this: As you work your way down and across the periodic table, atoms have more protons and electrons. Atoms of hydrogen have one of each, helium two, lithium three, and so on. Plutonium has 94. The protons (plus neutrons) pack into the nucleus, while the electrons successively fill available states, known as orbitals, outside the nucleus. Different orbitals, denoted with the letters *s, p, d,* and *f,* have different capacities, and it is the extent to which the outermost, or valence, orbitals are filled that determines an element's chemical properties and its position on the periodic table. Carbon atoms, for example, have four valence electrons and therefore four bonding sites, and correspondingly, they can form diamond, a four-sided crystal.

Against all odds, plutonium is the low-hanging fruit for studying electronic correlations.

This is basically the story of how the structure of the atom determines the behavior of the element. It's a great story, but it's not always complete. Rather, the structure of an atom can change in response to all the other atoms in a material, thereby changing the nature of the material itself. And a handful of material might contain trillions of trillions of atoms.

It is possible for neighboring atoms to reside far enough from one another that the valence electrons stay localized to their corresponding nuclei—roughly an ordered collection of isolated atoms. However, the atoms in a material can also lie so close to one another that the valence orbitals of neighboring atoms will overlap. In this latter case, it's often unclear which atom a particular valence electron should call home; therefore, some electrons are essentially free to wander through the material, making the material an electrical conductor (a metal). In the former case, where no electron is free to move away from its home atom, the material cannot conduct electricity and is called an insulator.

In the case of a conductor, however, additional complications arise. If each atom supplies, on average, one electron that's free to roam (or "itinerant"), then there will be as many itinerant electrons in the material as there are atoms. As they move through the material, they interact with one another (and with all the other electrons localized to their nuclei) via electrostatic repulsion (due to their negative charges) and via magnetic interactions (due to a combination of their negative



charges and their spins). So how do all these numerous and complicated electromagnetic interactions affect the behavior of a metal's itinerant electrons?

Luckily for physicists, it turns out that in simple metals, such as copper, these interactions are typically very weak and can be partially ignored. This is the basis for the Fermi-liquid theory, originally put forth in the 1950s, which is, in many ways, the standard model of solids. The theory describes the electrons in a solid as a collection of non-interacting "quasi-particles" that have the same properties as free electrons except for a slightly higher effective mass to account for their interactions with other electrons. Just as an Olympic sprinter would be slowed down by obstacles on the track, an itinerant electron is slowed down by other electrons in its path. And how much either one is slowed down can be approximated with additional mass instead of obstacles, as though the sprinter had packed on a few extra pounds over Thanksgiving and the electron had acquired a higher-than-textbook-value mass.

While this standard theory has been extremely successful for materials in which itinerant electrons undergo weak interactions, it fails to explain more complex materials. It fails spectacularly with plutonium.

One foot out the door

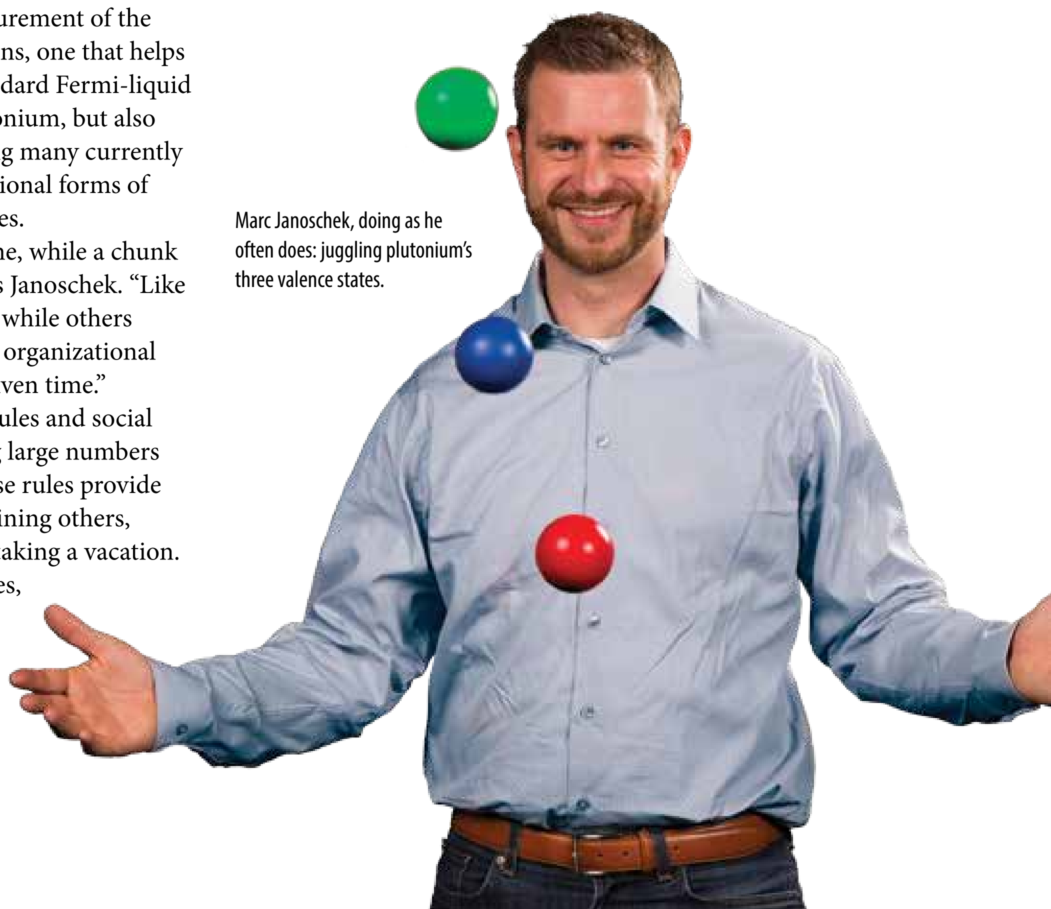
"The valence electrons of plutonium occupy a complicated no-man's land between localized and itinerant configurations," says Los Alamos's Marc Janoschek. Janoschek is the collaboration leader for a groundbreaking new measurement of the dualistic nature of plutonium's valence electrons, one that helps explain exactly how plutonium defies the standard Fermi-liquid theory. Yet this result applies not only to plutonium, but also to complex materials more generally, including many currently known materials that demonstrate unconventional forms of superconductivity and other electronic oddities.

"Think of an individual atom like a home, while a chunk of metal is like an entire community," explains Janoschek. "Like people, some electrons never leave the house, while others travel. And both communities respect certain organizational principles that affect who is traveling at any given time."

Human communities are organized by rules and social structures that promote efficiency by allowing large numbers of individuals to contribute to the whole. These rules provide standardized reasons for leaving home and joining others, such as going to college, moving for a job, or taking a vacation. Electron communities, too, follow certain rules, in which multiple electrons (or in some cases, all of them) act in concert. Just as people are better off in a rule-abiding community, electrons save energy by acting together. Evidence of such coordination among electrons, known as electronic correlations, is available from a zoo of exotic electronic behaviors discovered over the last few decades.

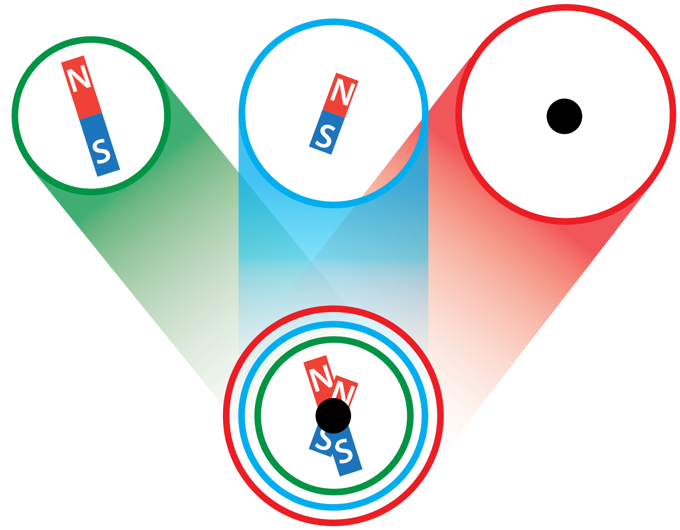
However, while the key role of electronic correlations in plutonium and other complex materials is well accepted among scientists, the exact rules that govern them—when valence electrons within the community are traveling versus staying home, or returning home, or visiting someone else's home—are not well understood. With simpler metals, it is often sufficient to imagine that one or more valence electrons effectively make a choice to stay home or wander off and stick with that choice, localized or itinerant, forever. If the latter, then scientists treat them like free electrons and assign them a higher effective mass. But for a valence electron in plutonium, the stay-or-go decision is eternally in flux and dependent on all its neighbors, which are also in flux—a much more complicated situation.

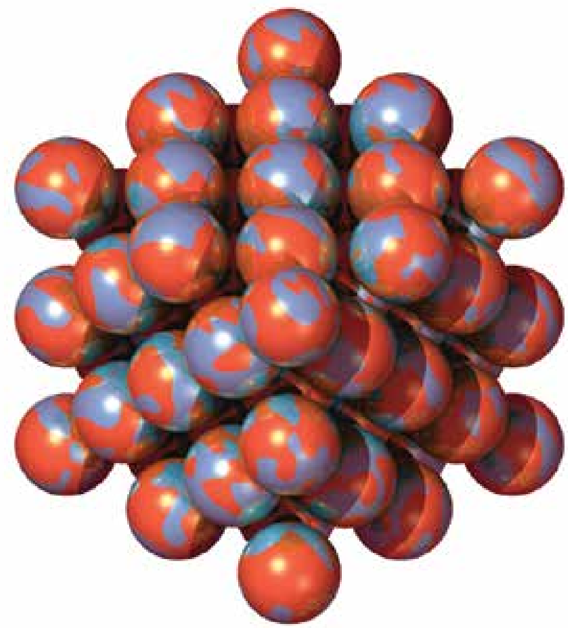
What motivates material scientists and physicists like Janoschek to study strong electronic correlations despite the challenges is that they frequently lead to material properties that are critical for future applications. These include exotic varieties of superconductivity, conducting electricity resistance-free even at relatively high temperatures and making possible such technological boons as levitating trains, faster computers, inexpensive MRI systems, lossless transformers and power transmission lines, and other energy applications. They also include a property called colossal magnetoresistance, in which



Marc Janoschek, doing as he often does: juggling plutonium's three valence states.

(Lower frame) The atoms in the delta phase of plutonium are arranged in a face-centered cubic structure. This simple, well-defined crystal arrangement and the absence of other contaminating elements make plutonium suitable for neutron scattering experiments. Valence electrons bound to each atom interact strongly with the free-to-roam sea of conduction electrons that permeates the solid metal. These interactions cause fluctuations in the state of each atom, resulting in some atoms keeping all their electrons and others giving up either one or two. (Center frame) Each atom is constantly shifting among these three states and thus exists nominally in a blend of all three, time-averaging the different properties of each state—including different atomic sizes and intrinsic magnetism (upper frame). Fluctuations between states therefore imply fluctuations in magnetic properties, suggesting that plutonium's "missing" magnetism isn't exactly missing; it's just dynamic.





electrical conductivity changes drastically in the presence of a magnetic field, allowing for new spintronic and magnetic-sensing devices. Even the material properties of otherwise simple permanent magnets defy explanation without broadly coordinated electronic correlations.

And then, of course, there's plutonium's missing magnetism. But when valence electrons are influenced by the entire electron community, their overall behavior changes, and the expectation of magnetism should change as well.

Not a home, a Kondo

In a way, plutonium defies periodic-table trends. Normally, for familiar metals with *d*-orbital valence electrons—like iron or gold or platinum—a higher atomic number means more protons and electrons, and the additional positively charged protons in the nucleus pull all negatively charged electrons inward to make the overall atom smaller. Conversely, for rare-earth metals with 4*f* valence electrons, the additional protons have minimal effect on the overall size of the atom because the 4*f* orbital resides close to the nucleus, and its additional electrons shield more distant electrons from the additional positive charges in the nucleus. But for actinide elements, which have 5*f* valence electrons, the two effects compete: atoms get smaller with greater atomic number up to a point and then suddenly become larger and stay roughly the same size thereafter. (Care to guess which element occupies that transition point?)

The size and configuration of the atom affect material properties in two ways. First, they determine the extent to which an atom's outer electrons mingle with those from neighboring atoms, affecting how likely the electrons are to leave home and therefore affecting electrical conductivity. Second, if one or more electrons do leave home, that changes the configuration of those that remain, causing their spins and orbital motions to align differently, affecting magnetism. So roughly speaking, a localized 5*f* valence electron participates in making the material magnetic, while an itinerant electron participates in making it metallic.

Earlier research revealed that plutonium's valence electrons live in an ever-shifting blend of three states: all valence electrons stay home, one leaves home, or, occasionally, two leave home. Theoretically, two of these states ought to be magnetic. But interestingly, in the third, valence electrons leave home and have the possibility of interacting with magnetism-causing electrons (attached to their home atoms) in a way that nullifies the role of both electrons. This is known as the Kondo effect. It was first observed in normal metals laced with magnetic, transition-metal impurities (e.g., iron). There, conduction and magnetism-causing electrons pair up and cancel each other out at the location of each magnetic impurity.

But plutonium is its own impurity—two of its valence states, anyway—and that means the Kondo effect is constantly at work everywhere throughout the metal. Which electrons do what becomes a group decision because a magnetic cancelation in one spot can cause a state change in another, which encourages a conduction electron somewhere else to settle down, and so on. It's a never-ending interplay of electronic correlations that reaches every corner of the metal. Indeed, measurements of abnormally large electron contributions to the specific heat of plutonium lend support to this interpretation of Kondo-effect electron pairing with especially strong electronic correlations.

A research team from Rutgers University working in collaboration with Janoschek's Los Alamos colleague Jianxin Zhu developed calculations to examine this interpretation using an advanced methodology known as dynamical mean-field theory (DMFT). In the calculation, they treated the plutonium atoms as Kondo impurities. They found that magnetic atoms should come and go, pointing this way and that, never achieving a coherent alignment of the kind found inside genuinely magnetic materials.

"That means plutonium's missing magnetism isn't missing at all; it's dynamic," says Janoschek. "It moves and changes, driven by an ever-changing valence configuration. That makes it all but impossible to measure, which explains why all the measurements keep turning up no magnetism."

So there it is: the Kondo effect, electronic correlations, DMFT calculations, and dynamic magnetism—a nice, consistent story. And it's something scientists can apply to create all manner of advanced materials for the future, perhaps even leading to a whole new kind of electronics. But is any of it actually true? According to the pesky scientific method that every good scientist insists on using, an all-but-impossible measurement is the only way to find out.

Isotopes and allotropes

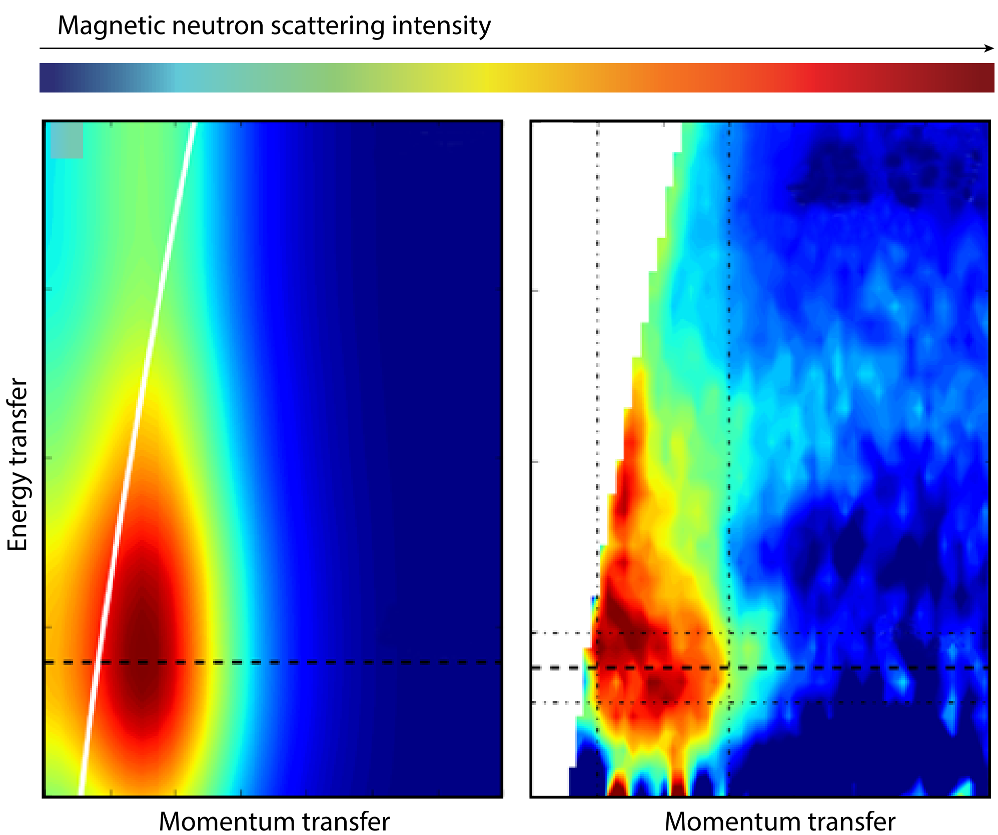
Janoschek decided to test the theory by bombarding a plutonium sample with neutrons to observe their deflection due to fleeting magnetic forces from the plutonium atoms. It's a straightforward experiment, one that's been tried before, but it can be riddled with confounding effects that must be painstakingly ferreted out.

Because neutrons carry a magnetic dipole moment, a property that makes them act like tiny compass needles, they are sensitive to magnetic forces. That much is good for the experiment, but unfortunately, plutonium nuclei strongly absorb neutrons, which induce the nuclei to split in the process known as fission. Most of Janoschek's impinging neutrons would get lost in fission reactions before their magnetic deflection could be observed.

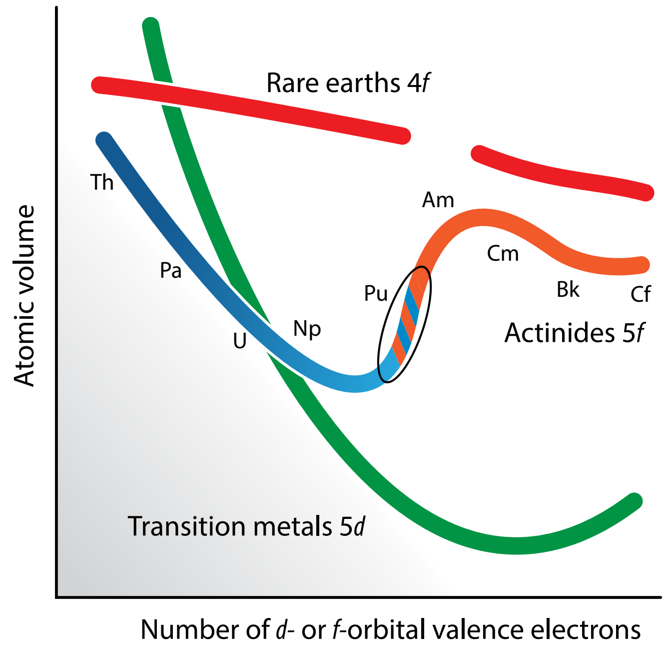
The standard theory to explain solids fails spectacularly with plutonium.

Help came from Los Alamos colleagues Eric Bauer, Jeremy Mitchell, Mike Ramos, and Scott Richmond, who knew how to prepare a sample made predominantly of plutonium-242, a rare, non-fissioning isotope with a far lower neutron-absorption rate than other isotopes. Bauer's research has been instrumental over the years in learning to work with plutonium-242. And because different isotopes of an element differ only in the number of uncharged neutrons in the nucleus, the behavior of their electrons is essentially identical.

After the neutron-absorption issue was solved, another confounding effect remained because, in addition to magnetic forces, neutrons are also deflected by nuclear interactions with protons and neutrons inside nuclei—from both the plutonium sample and its container. To tease out the magnetic effect, Janoschek repeated the experiment on a sample of thorium with the same crystal structure as plutonium. Since the nuclear properties of both elements are well known, it was possible to compare them to isolate and then subtract the effects of nuclear deflection. Similarly, he was able to subtract the contribution from the sample container (which, for safety reasons, is doubly



Intensity map of magnetic fluctuations causing neutron scattering with respect to the momentum (x-axis) and energy (y-axis) transferred to the neutron. The left frame shows the expected experimental outcome from dynamical mean-field theory calculations; the right frame shows the actual neutron scattering results.



The sizes of different atoms on the periodic table generally follow predictable patterns. The actinide series of elements, however, with valence electrons in the 5*f* orbital, mimics the pattern for transition metals up to a point and then abruptly changes to mimic the pattern for magnetic rare-earth elements. Plutonium straddles the divide.

thick for plutonium samples) by scattering neutrons against an empty one. None of this is as simple or straightforward as it may sound, and with perseverance and attention to detail, he completed the experiment and the analysis.

It was quite the moment of triumph and, Janoschek admits, no small amount of surprise, when the experiment confirmed theoretical predictions: the most numerous deflected neutrons had energies characteristic of the transition between valence states, and the strength of the magnetism producing the deflections agreed with the DMFT calculations. The all-but-impossible experiment had been pulled off, and just like that, a five-decade-old scientific mystery was no more.

In addition, Janoschek's experiment provides a firm new basis for understanding plutonium's extraordinary allotropes. Similar to carbon with its well-known graphite and diamond allotropes, solid plutonium can be reconfigured as well. But it has an astonishing variety of configurations, and they differ so dramatically that a change from one to another, brought about by a change in temperature, can make the metal grow or shrink by an incredible 25 percent.

Yet even this extreme behavior can be understood naturally in terms of plutonium's extreme, ongoing fluctuations in electron localization and delocalization. When electrons come and go and reconfigure, that changes the atoms' sizes and the angles at which they form chemical bonds. Some configurations allow the atoms to pack together tightly, like packing a box with small cubes. Other configurations waste space, like trying to pack the box with spheres instead, thereby expanding the volume. Combining plutonium's wildly shifting electron localization behavior with strong electron correlations throughout the material, it becomes easier to see how a temperature change might cause it to spontaneously reorganize in ways unmatched by other elements. And those reorganizations will naturally produce changes in material properties.

Strange bedfellows

It is perhaps a historical oddity that a new understanding of electronic correlations, both in terms of DMFT computations and neutron-scattering experiments, should come from plutonium. After all, this new understanding applies to a large number of materials, many of which, upon reengineering to take advantage of electronic correlations, are likely to offer greater societal rewards than plutonium. Yet the solution was discovered in plutonium, a nuclear weapons material available only to a small subset of scientists at a handful of high-security labs.

Plutonium, for all its complexity, happens to be the one material most suitable for this work. Against all odds, it is the low-hanging fruit for studying electronic correlations. It produces magnetic impurities and strong electronic correlations all by itself, without any other elements to complicate the analysis, and its delta-phase allotrope has a simple and regular cubic crystal structure. In these ways, plutonium makes both the theory and experiment accessible. And now that they are accessible, opportunities abound to develop electromagnetically ideal materials for novel magnetism- and superconductivity-based applications.

That isn't to say the benefits of this research reside exclusively outside the borders of the traditional plutonium-weapons world. One of Los Alamos's key charges is to develop the technology and expertise to protect the nation's nuclear weapons so that they remain safe and reliable over the decades. But aging plutonium—ravaged day by day by its own radioactivity—is even more perplexing than fresh plutonium, and keeping it under control is painstaking, diligent work. For those who do that work, there's tremendous potential to be found in the more comprehensive understanding of plutonium that Janoschek and his colleagues have now provided. For the wider electron-correlation research community, there's excitement and opportunity for advanced materials. And for everyone else, there can be an appreciation of progress—and perhaps a little relief. LDRD

—Craig Tyler